

The University of Chicago

I. THE SOLVENT EFFECT IN THE ADDITION
OF HYDROGEN BROMIDE TO ISOBUTYLENE

II. THE PEROXIDE EFFECT IN THE ADDITION
OF HYDROGEN BROMIDE TO ETHYLENE
COMPOUNDS. THE ADDITION OF HYDRO-
GEN BROMIDE TO THE HIGHER ALKENES

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1937

By

WILLIAM McDANIEL POTTS

Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

1939

The University of Chicago

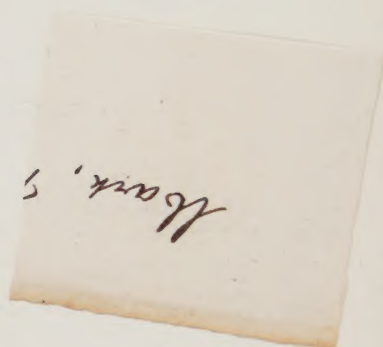
- I. THE SOLVENT EFFECT IN THE ADDITION
OF HYDROGEN BROMIDE TO ISOBUTYLENE
- II. THE PEROXIDE EFFECT IN THE ADDITION
OF HYDROGEN BROMIDE TO ETHYLENE
COMPOUNDS. THE ADDITION OF HYDRO-
GEN BROMIDE TO THE HIGHER ALKENES

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1937

By
WILLIAM McDANIEL POTTS

Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS
1939



ACKNOWLEDGMENT

I wish to acknowledge my indebtedness to Professor M. S. Kharasch for his kindly interest and encouragement during these researches. His invaluable suggestions and sympathetic understanding have been most helpful. I feel fortunate to have had the opportunity of working under his direction.



Digitized by the Internet Archive
in 2026

I. THE SOLVENT EFFECT IN THE ADDITION OF HYDROGEN BROMIDE TO ISOBUTYLENE

In a series of papers, Kharasch¹ and his students have reported the results of extensive researches on the addition of hydrogen bromide and hydrogen iodide to unsaturated compounds of the ethylene and acetylene series. In these papers, it has been shown that procedures are available for controlling the direction of addition to the unsaturated bond, so that either of two products may be obtained.

The nature of the product depends upon the procedure employed in the addition of hydrogen bromide. These two products are termed the normal and the abnormal products of the reaction. The normal product is the one predicted on the basis of the Markownikoff Rule and the abnormal product is the one which is formed in the presence of peroxides. To obtain a good yield of the normal product, all reagents must be peroxide-free and the system must be carefully evacuated so as to eliminate oxygen. Antioxidants are also added which seem to destroy the peroxide effect. The abnormal product of the addition of hydrogen bromide to the double bond is obtained in practically 100 per cent yields by the addition of a peroxide to the reaction mixture.

The solvent effect has been evaluated in several of these researches using a wide range of solvents and the conclusion was reached that with the exception of glacial acetic acid, the solv-

¹Kharasch and collaborators, J. Am. Chem. Soc., 55, 2468, 2521, 2531 (1933); 56, 244, 712, 1212, 1243, 1425, 1643, 1782 (1934); 57, 2463 (1935).

ent had no influence on the direction of addition of hydrogen bromide; its only effect was on the rate of addition in the peroxide-catalyzed reaction.

While Sherrell, Mayer, and Walter² were aware of these results, nevertheless they reported that the direction of addition of hydrogen bromide to pentene-1 and heptene-1 is controlled by the dielectric constant of the solvent. On the other hand, Kharasch, Hinckley, and Gladstone³ demonstrated conclusively that the addition of hydrogen bromide to pentene-1 is independent of the solvent. Sherrell, Mayer, and Walter⁴ concluded that due to the use of small quantities of reagents the results of these investigations were not significant; however Kharasch and McNab repeated the work on the addition of hydrogen bromide to propylene using relatively large quantities of reagents and they obtained excellent confirmation of their earlier results. Linstead and Rydon⁵ consider that the peroxide effect is of secondary importance in the addition of hydrogen bromide to allylacetic acid in hexane as the solvent, while Kharasch and McNab⁶ obtained results showing conclusively that the direction of addition to allylacetic acid is independent of the solvent.

The belief that the dielectric is the controlling factor in the addition of reagents to unsaturated compounds is held quite generally and is due in part to the fact that peroxide-free conditions are extremely difficult if not impossible of attainment in

²Sherrell, Mayer, and Walter, ibid., 56, 928 (1934).

³Kharasch, Hinckley, and Gladstone, ibid., 56, 1642 (1934).

⁴Sherrell, Mayer, and Walter, loc. cit.

⁵Nature, 132, 643 (1933); also Boorman, Linstead, and Rydon, J. Chem. Soc., 568 (1933).

⁶Kharasch and McNab, J. Chem. Ind., 54, 989 (1935).

the case of unsaturated compounds that show a high sensitivity to the peroxide effect. The vacuum technique with only the most highly purified reagents or the addition of small quantities of antioxidants to destroy the peroxide effect are the only methods now known which will eliminate this disturbing factor. The solvent and also the presence of impurities have probably influenced the rates of the "normal" and the "peroxide-catalyzed" reactions and these effects could easily account for some of the conclusions relating the solvent to the direction of addition.

Ingold and Ramsden⁷ have critically discussed the problem of the addition of reagents to the double bond and conclude that an alkyl group repels electrons and leads to the orientation $\text{RCH}(\text{x})\cdot\text{CH}_2(\text{H})$ and addition should be influenced to only a small extent by the medium. As far as the direction of addition is concerned, this explanation is in complete agreement with Kharasch's⁸ principle of "relative electronegativity of radicals." Further, Ingold and Ramsden conclude that reacting outside the molecule, R should repel electrons, anions, and the negative ends of polarized molecules, and should attract protons, cations, and the positive ends of polarized molecules. This tends to orientate $\text{RCH}(\text{H})\cdot\text{CH}_2(\text{x})$ and as this effect travels through the medium the nature of the medium should have a very great influence upon this effect; this external factor should be strongest in gas reactions, weaker in non-polar solvents and very weak in polar solvents.

Ingold and Ramsden conclude that the short distances involved in the addition of reagents indicate that other electrical phenomena are involved, while if distance as great as 100 Angstrom

⁷Ingold and Ramsden, J. Chem. Soc., 34, 2746 (1931).

⁸Kharasch and Reinmuth, J. Chem. Ed., 5, 404 (1928); 8, 1703 (1931).

units were involved the dielectric constant of the solvent could be used to measure the influence of the medium on the "externally propagated polar field." These other electrical phenomena include "electrical saturation effects, including influences due to electrostriction and molecular and field anisotropy, and the interactions of quadrupoles and higher multipoles with one another and with dipoles, and to distortion effects." The statistical calculation of these combined effects is not possible at present.

"These component forces all contribute to the internal pressures of liquids but so also does the effect of quantum-mechanical reciprocal perturbations."

These authors conclude that the dielectric constant takes account of too little and the internal pressure includes too much; therefore only a rough orientation with either property can be expected.

Mortimer⁹ lists the following values for the internal pressures of the following solvents: propane (0.56), nitrobenzene (1.07), acetic acid (1.95), water (4.60). If the direction of addition corresponds to the internal pressures, isopropyl iodide is the normal addition product of the addition of hydrogen iodide to propylene, while n-propyl iodide is the abnormal product; consequently more of the latter should be formed in propane and the smallest amount should be formed in water. Ingold and Smith¹⁰ observed this effect in the addition of hydrogen iodide to propylene, while Kharasch and Hannum observed only normal addition of hydrogen iodide to ethylenes and explained these results by the assumption that due to its reducing property hydrogen iodide

⁹Mortimer, J. Am. Chem. Soc., 44, 1416 (1922); 45, 633 (1923).

¹⁰Ingold and Smith, J. Chem. Soc., 34, 2742 (1931).

destroyed peroxides, thus preventing the formation of the peroxide-catalyzed product. Table 1 shows that in the addition of hydrogen bromide to isobutylene the normal addition does not correspond to the results predicted by the internal pressure series. A further study in the case of nitrobenzene as the solvent indicates that by suitable procedure it seems possible to obtain 100 per cent yields of the abnormal product. This procedure was largely for the purpose of securing a concentration of peroxide throughout the course of the reaction that would be sufficient to catalyze the addition reaction.

To further evaluate the solvent effect, an investigation was made of the addition of hydrogen bromide to isobutylene. Isobutylene was selected for this study as it had been shown by Kharasch and Hinckley¹¹ that "a variety of experimental conditions such as temperature, light, or solvent have no effect on the direction of addition of hydrogen bromide to isobutylene." They also found that 80 per cent yields of isobutyl bromide were obtained in the presence of peroxides and what is of greater importance, isobutylene does not form peroxides readily, thus indicating that good yields should be obtainable by the so-called "normal" addition and also that the peroxide effect could be demonstrated by the use of small quantities of peroxides.

In the previous work on the addition of hydrogen bromide to isobutylene, glacial acetic acid and xylene were the only solvents employed. To make a further investigation of the solvent effect, it was decided to carry out the addition of hydrogen bromide to isobutylene employing a number of solvents that showed a wide variation in the values of their dielectric constants and

¹¹Kharasch and Hinckley, J. Am. Chem. Soc., 56, 1243 (1934).

internal pressures. For convenience in carrying out these additions and in analyzing the products of the reactions, the following solvents were used: pentane (1.83), carbon disulfide (2.6), propionic acid (3.2), ethyl bromide (9.4), benzonitrile (26.4), nitrobenzene (36.1), and water (80). The dielectric constant of each solvent is indicated in parenthesis.

The technique employed in these additions was the same as that described in previous papers from this Laboratory. It should be pointed out, however, that the tubes containing the reaction mixtures were removed from the bath as soon as the seal had cooled, and that the contents soon reached room temperature. Even though some of the components may have solidified, this condition was only of short duration.

Two types of runs were made with each solvent; runs in which a peroxide (ascaridole) was added and the air was left in the tubes, and runs in which an antioxidant (diphenylamine) was used, and in these runs the tubes were evacuated to a pressure of 1×10^{-4} mm. while the reagents were frozen in liquid nitrogen baths.

The analyses of the products of the additions was effected by employing both the boiling points and the refractive indices. The index for tertiary butyl bromide is 1.4275-1.4277, and for the isobutyl bromide, 1.4355. In all experiments the composition of the mixture was made certain by repeated washing of it with sodium carbonate solution, and the determination of the index of refraction and boiling point of the dried material.

The results recorded in Table 1 show that the non-catalyzed peroxide-free addition is entirely independent of the solvent, since tertiary butyl bromide was the sole product in these cases. Since the solvents employed varied widely in the values of their

dielectric constants, from 1.83 to 80, it seems that there is sufficient basis for the generalization that neither the internal pressures nor the dielectric constants of the solvents have any influence on the direction of the addition of hydrogen bromide to isobutylene.

As has been mentioned previously, it seems that conditions can be obtained by which only the abnormal addition product is formed. While both addition reactions are quite rapid, the abnormal addition product is formed. While both addition reactions are quite rapid, the abnormal addition produced by peroxide catalyses does not appear to completely outrun the normal reaction. There is also the strong probability that appreciable quantities of the normal reaction product are formed in the period of time that elapses while the mixture is absorbing heat and during which time the solid reagents are undergoing transformations from the solid state. During this period it is quite likely that the ascaridole is inactive due to the fact that the mixture is inhomogeneous and the peroxide is probably not in solution at these low temperatures, but hydrogen bromide and isobutylene may be reacting and addition during this period would thus not be affected by the peroxide. It is within the range of possibility that the 100 per cent yield of isobutyl bromide in carbon disulfide may be due to the reaction taking place in a homogenous mixture of the solvent, catalyst, and reactants, thus being under the control of the peroxide effect during the entire period of the addition reaction

Summary

1. Pure tertiary butyl bromide is formed by the addition of hydrogen bromide in vacuo to isobutylene in the presence of antioxidants and solvents.

2. Isobutyl bromide is formed in amounts varying from 75 to 100 per cent by the addition of hydrogen bromide to isobutylene in the presence of solvents, air, and peroxides.

3. The conclusion is reached that under antioxidant conditions solvents have no influence on the direction of addition of hydrogen bromide to isobutylene, but affect greatly the rate of addition. This conclusion may be interpreted as indicating that the apparent effect of solvents on the direction of addition of hydrogen bromide is due to the influence of the solvent on the relative rates of the "normal" and peroxide-catalyzed addition reactions.

TABLE 1

ADDITION OF HYDROGEN BROMIDE TO ISOBUTYLENE IN SOLVENTS

A. Addition in the Presence of Peroxides									
Solvent	Pentane (1 M)	CS ₂ (1.2 M)	Propionic Acid (0.9 M)	Ethyl Bromide (1 M)	Benzo- Nitrile (0.7 M)	Nitro- Benzene (0.9 M)	Water (0.9 M)		
Ascaridole, M	0.03	0.04	0.04	0.03	0.04	0.04	0.04	13	0.04
Isobutylene {g. M}	17 0.3	13 0.23	15 0.27	12 0.21	11 0.20	13 0.23	13 0.23	25	0.23
HBr {g. M}	27.5 1.1	24 1.3	25 1.1	19 1.1	21 1.3	21 1.2	25 1.3	70-91.5	1.3
B.p. of reaction mixture, °C.	71.5-91.5	87.5-91	70-90	70-90	73-91.5	72-91	70-91.5	28.5	
Yield {g. %	33 79	26.5 86	31.5 86	26 88	20 74	29 94	28.5	92	
n ²⁰ _D	1.4338	1.4357	1.4345	1.4338	1.4338	1.4335	1.4345	13	
t-Butyl bromide, %	22	0	13	22	22	25	13	87	
Isobutyl bromide, %	78	100	87	78	78	75	87		
Reaction Mixture Washed with Sodium Bicarbonate and Water, Dried with Anhydrous Sodium Sulfate, and Distilled									
B.p., °C.	87-91	87-91	87-91	87-91	87-91	87-91	87-91	87-91	
n ²⁰ _D	1.4349	1.4354	1.4348	1.4351	1.4352	1.4348	1.4351	21	
Recovery of isobutyl g. bromide %	23 87	21 87	22.5 82	19 93	13 83	14 65	21 84	84	

TABLE 1--Continued

B. Addition in <u>Vacuo</u> and in the Presence of Antioxidants								
Solvent	Pentane (0.8 M)	CS ₂ (1.3 M)	Propionic Acid (1 M)	Ethyl Bromide (1 M)	Benzo- Nitrile (0.5 M)	Nitro- Benzene (0.9 M)	Water (1.5 M)	
Diphenylamine, M	0.03	0.03	0.03	0.03	0.03	0.04	0.03	
Isobutylene {g. M	13.5 0.24	12.5 0.22	12.5 0.22	13.5 0.24	10.5 0.19	12 0.21	20.5 0.37	
HBr {g. M	23.5 1.2	22 1.2	20 1.1	24 1.2	18 1.1	23 1.3	35 1.2	
B.p. of reaction mixture, °C.	69-73	52-72	69-73	63-73	71.5-72.8	73-73.3	71.5-72.8	
Yield {g. %	27.5 83	25.5 83	28 92	27.5 83	22 86	23.5 80	42.5 85	
n _D ²⁰	1.4267	1.4278	1.4278	1.4271	1.4272	1.4278	1.4271	
Reaction Mixture Washed with Sodium Bicarbonate and Water, Dried with Anhydrous Sodium Sulfate, and Distilled								
B.p., °C.	72.5-72.7	71.5-72.1	72-72.7	72-73	71.5-72	71.6- 72.6	72.2-72.5	
n _D ²⁰	1.4267	1.4278	1.4275	1.4270	1.4271	1.4273	1.4271	

II. THE PEROXIDE EFFECT IN THE ADDITION OF HYDROGEN BROMIDE TO ETHYLENE COMPOUNDS. THE ADDITION OF HYDROGEN BROMIDE TO THE HIGHER ALKENES

Introduction

The addition of hydrogen bromide to ethylene and acetylene compounds, in the presence and absence of peroxides, has been investigated in this laboratory.¹ It has been shown that in the absence of peroxides (and/ or oxygen), hydrogen bromide adds to unsaturated compounds to yield secondary bromides. On the other hand, in the presence of peroxides the normal bromides are formed. The previous studies were confined to the lower alkenes. It was of interest and of considerable theoretical moment to determine whether or not the same generalizations would apply to higher alkenes containing terminal double bonds. Through the kindness of Professor E. Emmet Reid of Johns Hopkins University, a number of long-chain unsaturated compounds, containing terminal double bonds, were made available to us. The quantities of these unsaturated substances were not very large, and an exhaustive study with each individual compound was impossible. In the main, however, the results obtained with nonene-1, tridecene-1, undecene-1, and heptadecene-1 indicate beyond a doubt that the generalizations, evolved as a result of the study of the short-chain unsaturated compounds, apply to the higher alkenes also.

¹Kharasch and others, J. Am. Chem. Soc., 55, 2468, 2521, 2531 (1933); 56, 244, 712, 1212, 1243, 1425, 1643, 1782 (1934); 57, 2463 (1935).

Discussion of Results

The results obtained, in the addition of hydrogen bromide to the higher alkenes, are given in Table 2. I have recorded the results obtained with all the samples sent us by Professor Reid. The available quantities of some of them, however, were so small, and the purification so difficult, that I have serious doubts whether any significance should be attached to the experiments with heptadecene-1, nonadecene-1, 4-phenylbutene-1, and 6-phenylhexene-1. The data obtained are included along with our other results, because Professor Reid has prepared solid condensation products of these bromides with phenolic compounds.

The addition of hydrogen bromide to the first five unsaturated compounds recorded in Table 2 is very fast, under "peroxide" as well as under "antioxidant" conditions. These high rates of addition, coupled with the presence of quantities of peroxides in the unsaturated compounds, make it extremely difficult to obtain quantitative yields of either the primary or the secondary bromides.

Unfortunately, since there was no ready analytical method to determine the percentage of primary and secondary bromides in the "peroxide" experiments, I was unable to adjust the conditions properly to take into account the enormously high rate of the "normal" addition. Had I been aware of that, I would have employed larger quantities of peroxides, and introduced the hydrogen bromide into the reaction mixture at a very slow rate. The results given in Table 2, therefore, are to be looked upon not as a record of what may be accomplished, but rather as a report of what the first trial experiments have yielded. Yet, the results obtained are of considerable significance. One may complain of

the yield, but there is no doubt that primary bromides are formed from the unsaturated compounds in the presence of peroxides, and that, therefore, the Markownikoff Rule applies not only to the short-chain unsaturated substances, but to the higher alkenes. The minimum yields of the primary bromides given in the table are taken from Professor Reid's paper. It should be emphasized that the 82 per cent of the primary bromide from nonene-1, 65 per cent, 60 per cent, and 41 per cent from undecene-1, pentadecene-1, and tridecene-1, respectively, are the minimum amounts of the primary bromides formed when hydrogen bromide is added to the unsaturated compounds under peroxide conditions.

Better results, than those given in the table, were obtained recently in the addition of hydrogen bromide to tri-decene-1.² The precaution was taken to insure the presence of about 10 per cent of peroxides in the reaction mixture. The hydrogen bromide was introduced slowly, in accordance with the procedure used by Kharasch and Hinckley.³ Under these conditions a product was obtained, which contained over 85 per cent of the primary bromide. The identification was first attempted through the conversion of the bromides obtained from "peroxide" and "anti-oxidant" experiments to the corresponding mercury compounds. No decisive results were obtained. The melting points of the mercury compounds of the primary and secondary bromides were very close (88° and 90° respectively), although each depressed the melting point of the other (79° - 80°). The identification was finally made through the condensation of the Grignard reagent of

²This result is reported separately in order not to cause confusion with the first sample analyzed by Professor Reid, and recorded in his publication.

³Kharasch and Hinckley, J. Am. Chem. Soc., 56, 1212 (1934).

the supposedly primary bromide with phenyl isocyanate. An anilide was obtained which melted at 80° - 82° , and the melting point of it was not depressed by the addition of a synthetic sample of myristic anilide.

Summary

1. It has been shown that the addition of hydrogen bromide to the higher alkenes, containing terminal double bonds, results in the formation of primary bromides, whenever "peroxides" are present in the reaction mixture, while secondary bromides are formed in the presence of "antioxidants."

2. The validity of the Markownikoff Rule as applied to long-chain unsaturated hydrocarbons has been confirmed.

TABLE 2

ADDITION OF HYDROGEN BROMIDE TO HIGHER ALKENES

Hydrocarbon	"Antioxidant" Conditions		"Peroxide" Conditions		% Primary Bromide Estimated by Prof. Reid
	B. P.	N _D ²⁰	B. P.	N _D ²⁰	
1. Nonene-1	63-67 ₄ mm.	1.4542	71-75 ₆ mm.	1.4529	82+
2. Undecene-1	100-101 ₅ mm.	1.4567	98-99 ₅ mm.	1.4557	65+
3. Tridecene-1	129-131 ₅ mm.	1.4574	121-123 ₅ mm.	1.4568	41+
4. Pentadecene-1 ..	142-147 ₆ mm.	1.4604	130-131 ₆ mm.	1.4592	60+
5. Allyl benzene ..	98-102 ₆ mm.	1.5457	91-93 ₆ mm.	1.5449	See Dr. Reid's paper
6. Heptadecene-1 ..	163-165 ₆ mm.	1.4616	158-160 ₆ mm.	1.4606	..
7. Nonadecene-1 ...	191-195 ₆ mm.		185-186 ₆ mm.		..
8. 4-Phenylbutene-1	108-109 ₆ mm.	1.5392	102-103 ₆ mm.	1.5358	..
9. 6-Phenylhexene-1	129-133 ₆ mm.	1.5273	115-118 ₆ mm.	1.5280	..

